First Examples of Resolved Enantiomeric Chromium(0)

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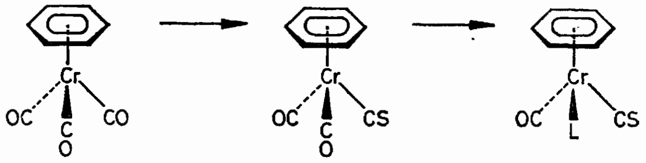
Summary The resolution of chiral chromium centres generated from optically active arene tricarbonyl chromium precursors is presented.

Certain chromium carbonyl complexes are excellent, selective catalysts for polymerisation and hydrogenation reactions.[1] Most of the previous studies have used arene tricarbonyl chromium(0) complexes, but the use of similar complexes having the requisite electronic properties and containing chiral chromium centres offers the possibility of catalytic asymmetric syntheses under mild conditions. We now report the first examples of resolved and stable chromium(0) complexes which owe their optical activity to the chiral chromium centre. Optically active pseudotetrahedral metal(0) centres have been reported for other metals,[2] but in very few cases do the complexes derive their chirality from an asymmetric metal centre alone.



Scheme 1

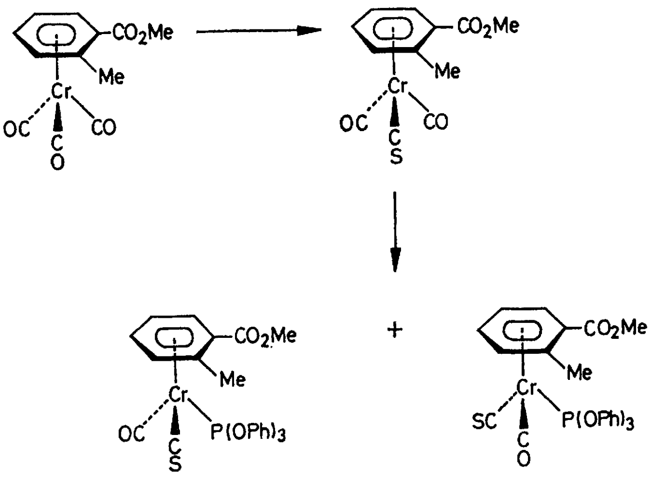
Table

L	PPh_3	$P(OEt)_3$	$P(OMe)_3$	$P(OPh)_3$	CO	CS
ν_{CO}/cm^{-1} [a]	1871 1923	1876 1927	1877 1930	1893 1944	1928 1994	1939 1992
Force constants *k* md $Å^{-1}$	14·53	14·60	14·63	14·87	15·36	15·60

[a] Beckmann I.R. 12 (CCl_4).

The chiral chromium centre is obtained by substitution of the parent tricarbonyl complex by two other and dissimilar ligands. Ligands can be found which give disubstituted complexes which are both thermally and optically stable in solution. Our synthetic technique is based on the fact that CS is more strongly bonded to chromium than CO, and thus, under photochemical conditions, phosphite substitution of the dicarbonyl, thiocarbonyl compound proceeds with selective removal of CO (Scheme 1).[3]

From optically pure 1-*S*-[1-CO_2Me,2-Me-(η^6-C_6H_4)]Cr-$(CO)_3$,[4] m.p. 86°, $[\alpha]^{25}_{D}$ + 103° (*c* 2·20 g l^{-1}; $CHCl_3$) we obtained 1-*S*-[1-CO_2Me,2-Me(η^6-C_6H_4)]Cr$(CO)_2$CS, m.p. 76°, $[\alpha]^{25}$ +192° (*c* 2·08 gl^{-1}; $CHCl_3$), $\tau(CD_3COCD_3)$ 7·47 (s,Me) and 6·07 (s, CO_2Me); and then [1-CO_2CH_3, 2-Me(η^6-C_6H_4)]Cr(CO)(CS)P$(OPh)_3$ (Scheme 2).



(1) + (2) $[\alpha]^{25}_{D}$ +60°

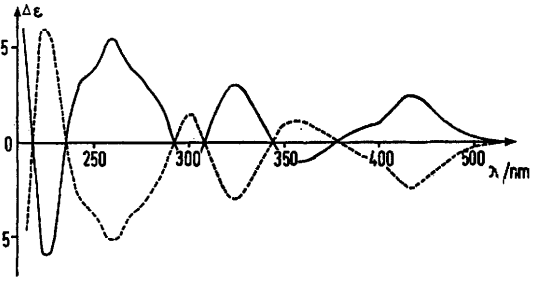
Scheme 2

We initially obtained the enantiomeric chromium complexes as their internal diastereoisomers (**1**) and (**2**) which are produced in approximately equimolar amounts. They were separated by t.l.c. on silica gel using 90:10 hexane-benzene as eluant. [(**1**) m.p. 133° $[\alpha]^{25}_{D}$ + 161° (*c* 1·5 g l^{-1}; C_6H_6), τ (C_6D_6) 6·57 (Me), and 7·63 (CO_2Me); (**2**) m.p. 111°, $[\alpha]^{25}_{D}$ −36° (*c* 1·5 g l^{-1}; C_6H_6), τ (C_6D_6) 6·52 (Me) 7·84 (CO_2Me)].

The enantiomeric complexes were then generated by removal of the planar chirality afforded by the substituted arene ring. This was accomplished by $LiAlH_4$–$AlCl_3$ reduction of the ester function in (**1**) and (**2**). The resultant enantiomeric complexes (**3**) and (**4**) show equal and opposite rotation [(**3**), m.p. 140°, $[\alpha]^{25}_{D}$ + 173° (*c* 1·5 g l^{-1}, C_6H_6), τ (CD_3COCD_3) 8·22 and 8·09 (Me); (**4**), m.p. 140, $[\alpha]^{25}_{D}$ − 171° (*c* 1·5 g l^{-1}, C_6H_6), τ (CD_3COCD_3) 8·22 and 8·09 (Me)]. We can therefore conclude that no racemization occurs during reduction of the diastereoisomers and that the optical purity of each is identical to that of the starting material, *i.e.* 100%, as previously established.[4]

The optical rotations and c.d. spectra (Roussel-Jouan model B, dioxan) of solutions of (**3**) and (**4**) are unchanged after several days (20°) (Figure).

With ligands other than $P(OPh)_3$, *e.g.* PPh_3 and $P(OEt)_3$, we have also obtained optically stable chiral chromium complexes similar to (**3**) and (**4**) but so far in lower optical purities (14—33%) due to problems associated with separating the diastereoisomers.



Figure

The donor properties of $P(OPh)_3$ approximately compensate the acceptor properties of CS such that (**3**) and (**4**) closely resemble the parent tricarbonyl *i.e.* electron density at the metal is similar (Table 1).

The relationship between the electron density on the metal and the i.r. stretching frequency of the carbonyl ligands has been previously established for this type of complex.[3] Variation in CO stretching frequencies between related molecules of different symmetry can be rationalized using the Cotton-Kraihanzel equation.[5] It is clear from the Table that the average force constant calculated for the $(CO)_2P(OPh)_3$ and $(CO)_2$ CS complexes is very close to that for the $(CO)_3$ complex.

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[1] M. F. Farona, P. A. Lofgren, and P. S. Woon, *J.C.S. Chem. Comm.*, 1974, 246; E. N. Frankel and R. O. Butterfield, *J. Org. Chem.*, 1969, **34**, 3930; M. Cais and A. Rejoan, *Inorg. Chim. Acta*, 1970, **4**, 509; G. Platbrood and L. Wilputte-Steinert, *J. Organometallic Chem.*, 1974, **70**, 393.

[2] H. Brunner, *Angew. Chem. Internat. Edn.*, 1971, **10**, 249; H. Brunner, VIth Internat. Conference Organometallic Chem., Amherst, 1973.

[3] G. Jaouen and R. Dabard, *J. Organometallic Chem.*, 1974, **72**, 377.

[4] R. Dabard, A. Meyer, and G. Jaouen, *Compt. rend. Series C*, 1969, 286, 201; G. Jaouen and R. Dabard, *J. Organometallic Chem.*, 1970, **21**, 43.

[5] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432; M. Herberold and C. R. Jablonski, *Inorg. Chim. Acta*, 1974, **7**, 241.